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RADIATION CHEMISTRY LABORATORY SERIES

RESEARCH REPORT NO. 7

61-3-2

XEROX

IRRADIATION "FACTOR-DEPENDENCY"

Some Vinyl Monomers: Multiple Parameters

QUARTERMASTER RESEARCH & ENGINEERING CENTER

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FOREWORD

This report, Research Report No. 7, Irradiation "Factor-Dependency," Radiation Chemistry Laboratory Series, deals with multiple factors such as the use of air, vacuum and various combinations of flame-out of the tubes and degassing of the monomer.

Data of Research Report No. 1, Styrene, indicate that factors such as atmosphere, degassing, diluent, dose, dose rate, moisture, and temperature all appear to be important parameters. Atmosphere, dose rate, and temperature were found to be statistically significant, with variations in dose rate being approximately twice as effective as variations in either atmosphere or temperature. With respect to molecular weight, temperature was found to be statistically significant at dose rates of 25,000, 50,000, and 100,000 rads per exposure. The non-additivity of dose was reported.

Research Report No. 2, Some Vinyl Monomers, gave results which indicate that under the experimental conditions employed: (1) polymerization rate is not equal to $kI^{1/2}$, (2) the E-value ("G_e"-value or amount of polymer obtained per unit of radiation energy) decreases with an increase in dose rate, (3) there is a non-additivity of dose, and (4) unless parameters are critically defined, the formulation of reaction rate has no significance.

Research Report No. 3, Styrene with Additives, provided data from which it was concluded for the additives used that: (1) the effect of an additive is a function of dose rate with respect to both molecular weight and conversion to polymer, and may either catalyze or inhibit polymer formation, (2) the molecular weight decreases with an increase in dose rate for all additives used, (3) there appears to be an inverse ratio with respect to conversion and molecular weight, and (4) the efficiency of polymerization decreases markedly at the higher dose rates used in these studies.

In Research Report No. 4, Irradiation Cycle, it was concluded that: (1) a cycle of something more than three minutes at 75°C. is the most efficient for the irradiation-induced polymerization of certain vinyl monomers, (2) the better relative efficiency of a time cycle over continuous irradiation decreases with an increase in dose rate, (3) efficiency decreases markedly at the higher dose rates used in these studies, (4) reaction rate formulations, derived under experimental conditions different from those used in this study, are not applicable, and (5) the most desirable time cycle and temperature are functions of the monomer system.

Research Report No. 5, Degassing, presented experimental results from which it was concluded that: (1) degassing may significantly increase the conversion to polymer obtained by the irradiation-induced polymerization of vinyl monomers, and (2) the relative importance of degassing is interdependent on (a) the monomer system, (b) the dose rate, and (c) in certain cases at least, the presence of an inert atmosphere such as argon.

From data on the composite effect of degassing and the irradiation cycle, Research Report No. 6, it was concluded that: (1) with the other parameters used in this study, an irradiation cycle of more than three minutes is required for optimal conversion to polymer at a given dose rate and dose level, (2) both the effect of degassing and the irradiation cycle are dependent to some extent on the monomer system, (3) degassing is more dependent, with respect to its effect, on the monomer system than is the irradiation cycle, and (4) the relative composite effect of degassing and the irradiation cycle decreases in general with an increase in dose rate and total dose.

Table of Contents

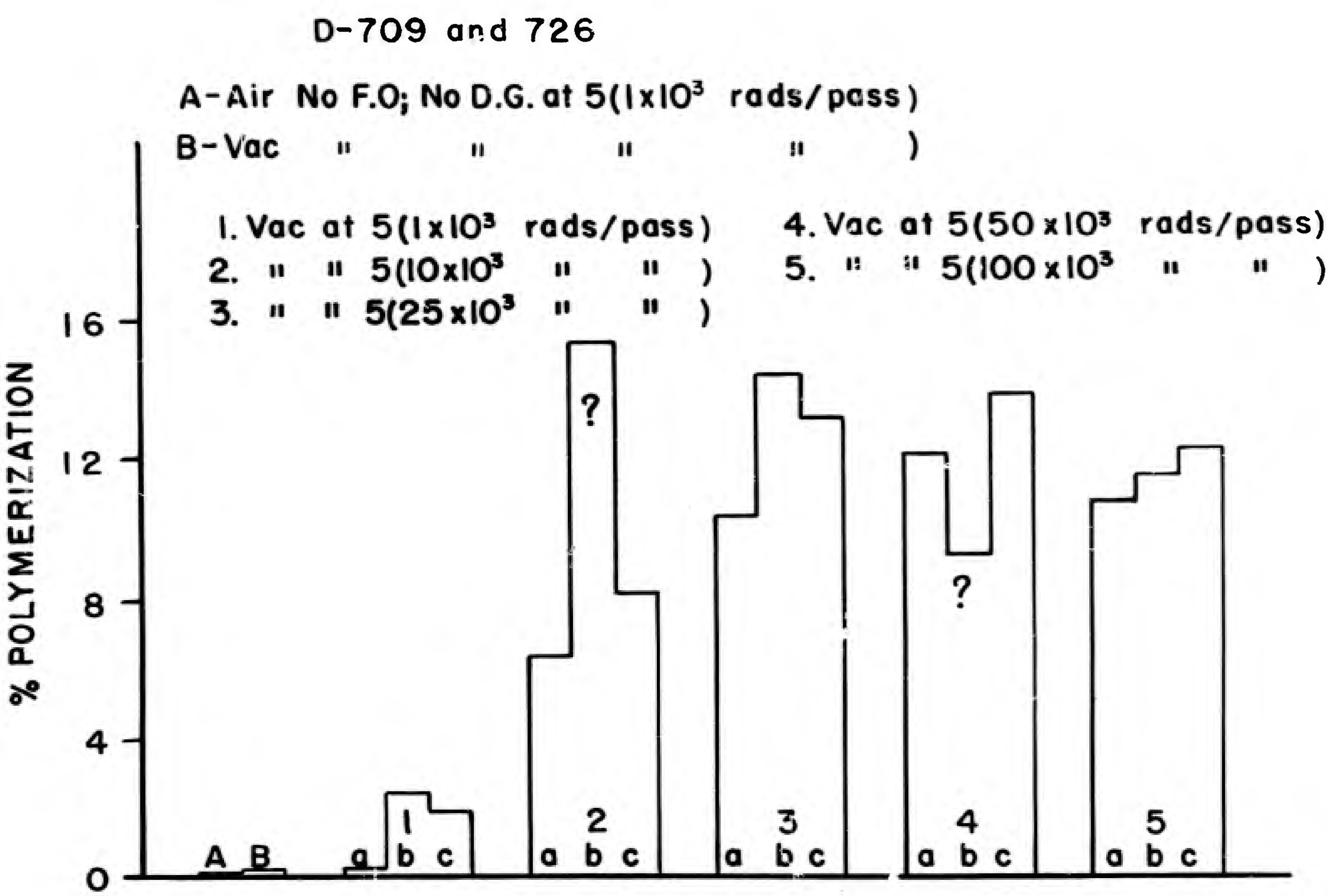

Figure 1. Acrylonitrile: Multiple-Degassing Effect (D-709 and 726). Values for comparable-heat control samples for A and B are 0.0% and 0.0%.

Irradiation "Factor-Dependency": Multiple Factors

By Ed. F. Degering, Flora E. Evans, and Stephen Grib

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A. Introduction

The experimental results reported herein represent relative rather than absolute values (cf. Research Reports, Nos. 3 and 4, Section A).

In Research Report No. 6 consideration was given to both the composite effect of degassing of the monomer prior to irradiation and to the irradiation cycle. In the present report data for the effect of fifteen factors, singly or combined, are presented.

B. Preparation of Samples

The meticulous procedure developed in the Radiation Chemistry Laboratory for the preparation of monomer samples for irradiation (Section B of Research Reports Nos. 4 and 5) was used for the experiments reported herein.

The monomer systems used in this study were acrylonitrile, butyl acrylate, styrene, vinyl acetate, acrylonitrile-styrene (1:1, v:v), butyl acrylate-styrene (1:1, v:v), vinyl acetate-styrene (1:1, v:v), acrylonitrile-vinyl acetate (1:1, v:v), butyl acrylate-vinyl acetate (1:1, v:v), and 1,1,3-trihydroperfluoropropyl acrylate.

Two series of monomers were prepared and irradiated. In series I, the A-samples were prepared with an atmosphere of air in the tubes, the tubes were not flamed out, and the monomer was not degassed; and the B-samples were frozen with liquid nitrogen, in tubes which were not flamed

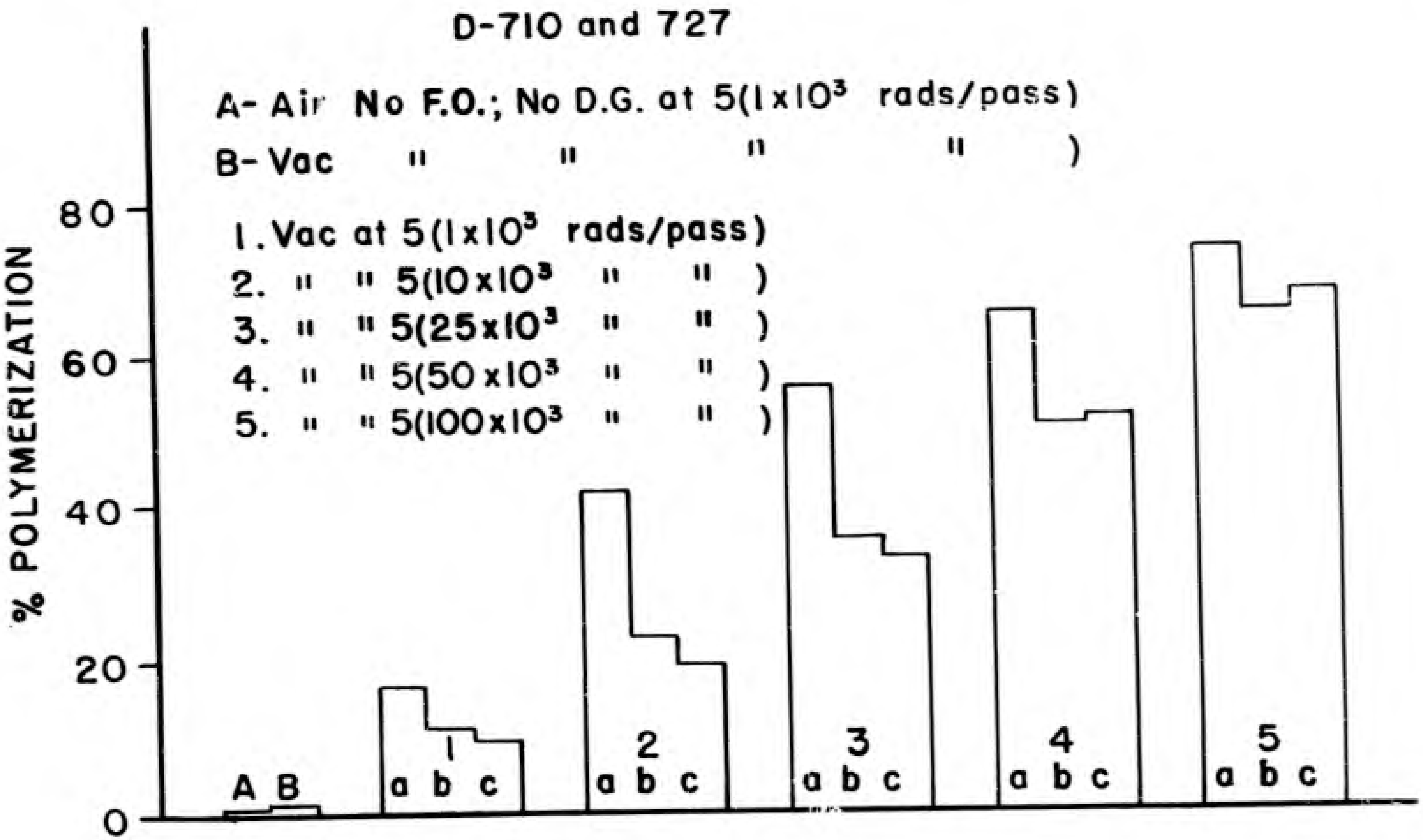


Figure 2. Butyl Acrylate: Multiple-Degassing Effect (D-710 and 727). Comparable heat-control values for A and B are 0.0% and 0.0%.

out, the monomer was not degassed, and the tubes were evacuated to five microns and sealed off for subsequent irradiation.

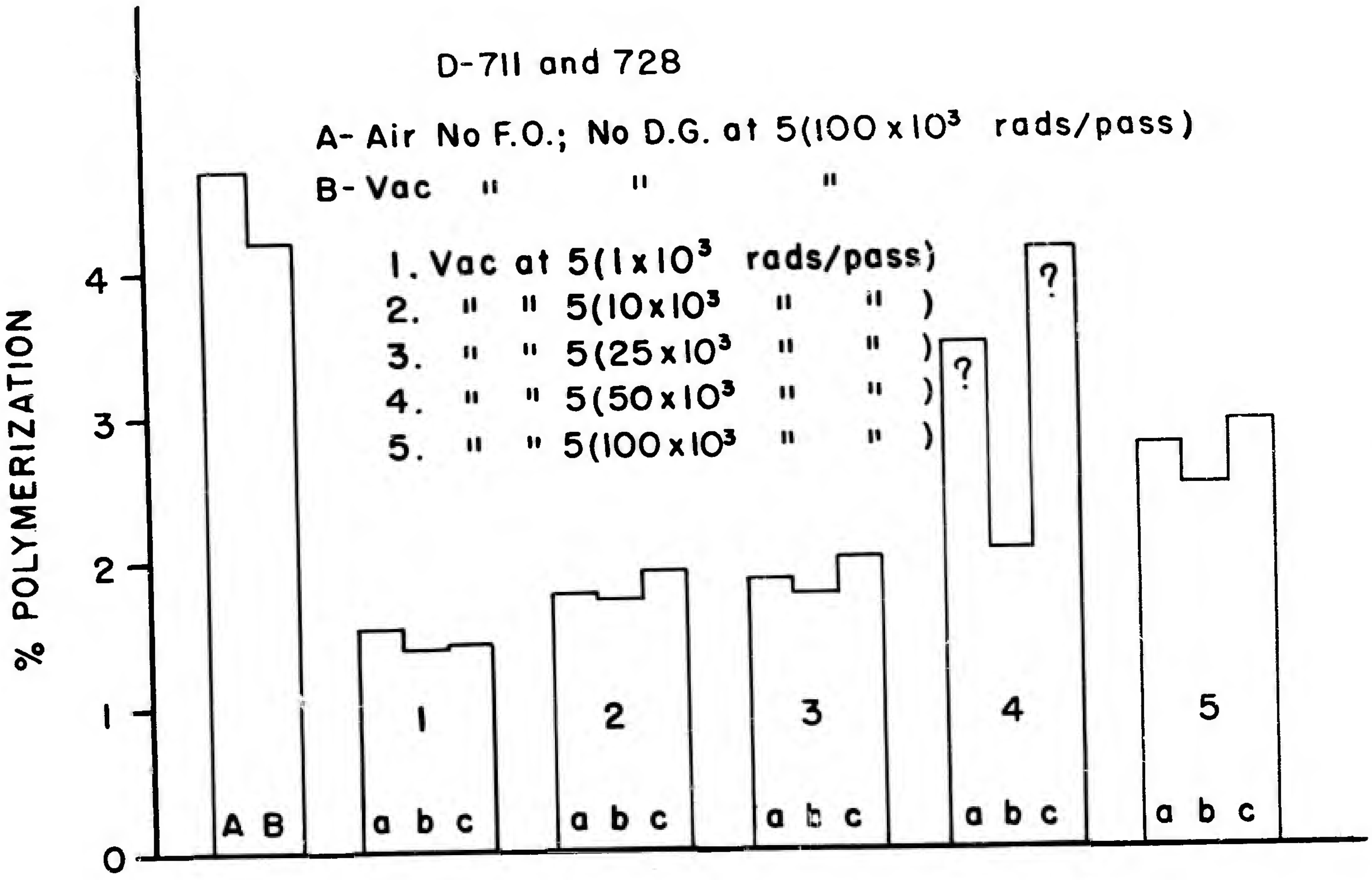
Five additional groups of samples of series I, nine tubes in each, were prepared for irradiation at dose rates of 1,000 rads per exposure on a forty-five-minute cycle at 75°C., and similarly for 10,000, 25,000, 50,000, and 100,000 rads per exposure. All of the tubes for these five groups were flamed out three times, with the final flame-out being effected at five microns. The samples were frozen with liquid nitrogen, degassed, and the tubes sealed off. The a-samples of each group (three each) were subjected to one degassing, the b-samples to two degassings, and the c-samples to three degassings.

In series II, 30 samples were prepared for each of the monomer systems. The conditions considered were: (1) air, no flame-out, no degassing, (2) vacuum, no flame-out, no degassing, (3) vacuum, three flame-outs, no degassing, (4) vacuum, no flame-out, one degassing, (5) vacuum, three flame-outs, one degassing, (6) vacuum, three flame-outs, two degassings, (7) vacuum, three flame-outs, three degassings, and (8) also vacuum, three flame-outs, three degassings. Samples were prepared also as heat controls for each of the monomer systems for conditions 1, 3, and 7.

C. Irradiation of Samples

The samples considered in this report were irradiated on a forty-five-minute cycle at 75°C. by use of a $1\frac{1}{2}$ Mev electron accelerator (Van de Graaff), operating at 2 Mev.

The samples for Figures 1 to 7 were irradiated at five different dose rates, namely, 1,000, 10,000, 25,000, 50,000, and 100,000 rads per exposure and to a total dose respectively of 5,000, 50,000, 125,000, 250,000, and 500,000 rads. The samples for each of the other figures (Figures 8 to 15) received five exposures each at dose rates as follows:



<u>Figure 3.</u> **Styrene: Multiple-Degassing Effect (D-711 and 728). Values for comparable heat-control samples for A and B are 0.3% and 1.1%.**

acrylonitrile (Figures 8 and 9), 1,000 rads per pass, butyl acrylate (Figure 10), 1,000, styrene (Figure 11), 100,000, vinyl acetate (Figure 12), 10,000, acrylonitrile-vinyl acetate (1:1, v:v, Figures 13 and 14), 10,000, butyl acrylate-vinyl acetate (1:1, v:v, Figure 15), 25,000, styrene-vinyl acetate (1:1, v:v, Figure 16), 100,000, and 1,1,3-trihydroperfluoropropyl acrylate (Figure 17), 1,000 rads per exposure.

D. Processing of Samples

The procedure developed by the Radiation Chemistry Laboratory for the processing of samples of irradiated monomer systems is discussed in some detail in Research Report No. 3, Section D, page 13, November, 1960, and in Research Report No. 4, Section D, page 7, December, 1960.

E. Experimental Results

The results obtained for seven monomer systems at the five dose rates and five dose levels are shown as the bar graphs of Figures 1 to 7. The A-bar of each graph is the average for samples which were irradiated in an atmosphere of air and in tubes which were not flamed out and from samples which were not degassed. The B-bar of each graph represents a comparable value for samples which were frozen and evacuated to five microns before sealing off for irradiation. The a-bars are for values from samples which were degassed once, the b-bars for those which were degassed two times, and the c-bars for samples which were degassed three times.

1. The Acrylonitrile Systems:

The data obtained for acrylonitrile (Figure 1, page iv) indicate that a second degassing contributes in general to polymer formation. These results lead to the conclusion that the degassing effect is a function of the dose rate. The effect of degassing is confirmed by the data of Figures 8 and 9 (pages 12 and 13), in which eight variations in parameters are used at one dose rate and at one dose level.

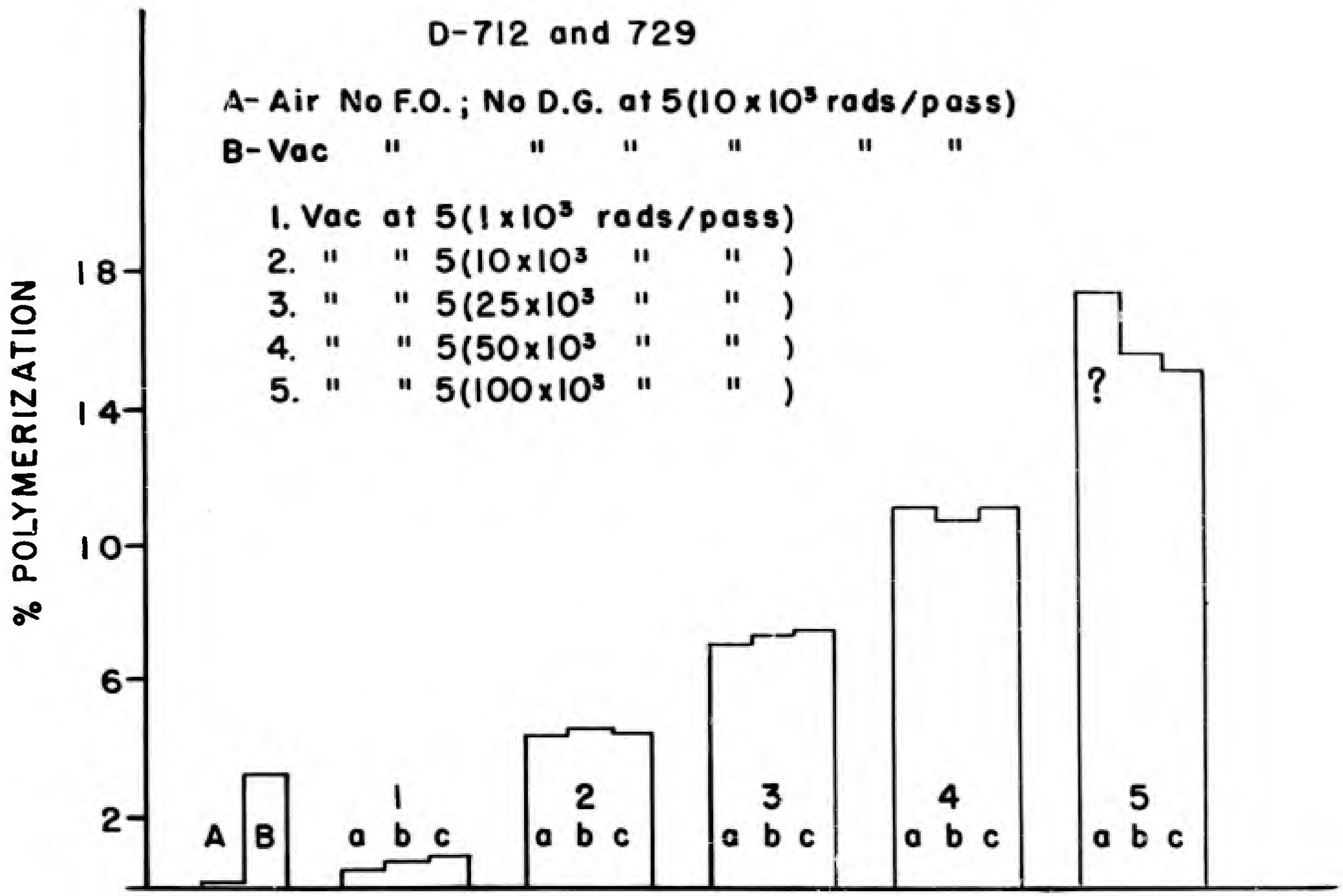


Figure 4. Vinyl Acetate: Multiple-Degassing Effect (D-712 and 729). Values for comparable heat-control samples for A and B are 0.0% and 0.0%.

There is a consistent increase in polymer yield in going in turn from the use of air with no flame-out and no degassings, to vacuum with no flame-out and no degassing, to vacuum with three flame-outs and no degassing, to vacuum with no flame-out and one degassing, to vacuum with three flame-outs and one degassing, to vacuum with three flame-outs and two degassings, and to vacuum with three flame-outs and three degassings. There is a very significant decrease in conversion, however, when three flame-outs and three degassings are used at 25°C. for the irradiation instead of at 75°C. (cf. bars 7 and 8 of Figure 8). This confirms previous observations that there is a significant synergistic effect between the use of heat and the appropriate combination of other parameters. Further study of this system is indicated.

The photograph of the irradiated reaction tubes for the acrylonitrile system (Figure 9, page 13), is included to present a visual indication of the effects of a variation in parameters. The parameters used for the various tubes are given in the legend. The weight of polymer obtained per tube, left to right, was: 0.0%, 0.01%, 0.3%, 1.1%, 1.5%, 3.1%, 3.9%, 4.4%, and 0.3%.

2. <u>The Butyl Acrylate Systems</u>:

The data obtained for butyl acrylate (Figure 2, page 2) show a consistent increase in conversion to polymer for one degassing at the five dose rates used in this study. The second and third degassings, however, effected the formation of less polymer at the five dose rates than was obtained by one degassing. This suggests that a limited amount of oxygen might be desirable in the irradiation-induced polymerization of butyl acrylate with the parameters employed. Confirmation of this concept is evident from bars 5, 6, and 7 of Figure 10 (page 14), where dose rate is maintained at 1,000 rads per exposure for a total of five passes, and the parameters are varied through eight combinations. A comparison of bar 4 with bar 5 suggests that a trace of moisture might be

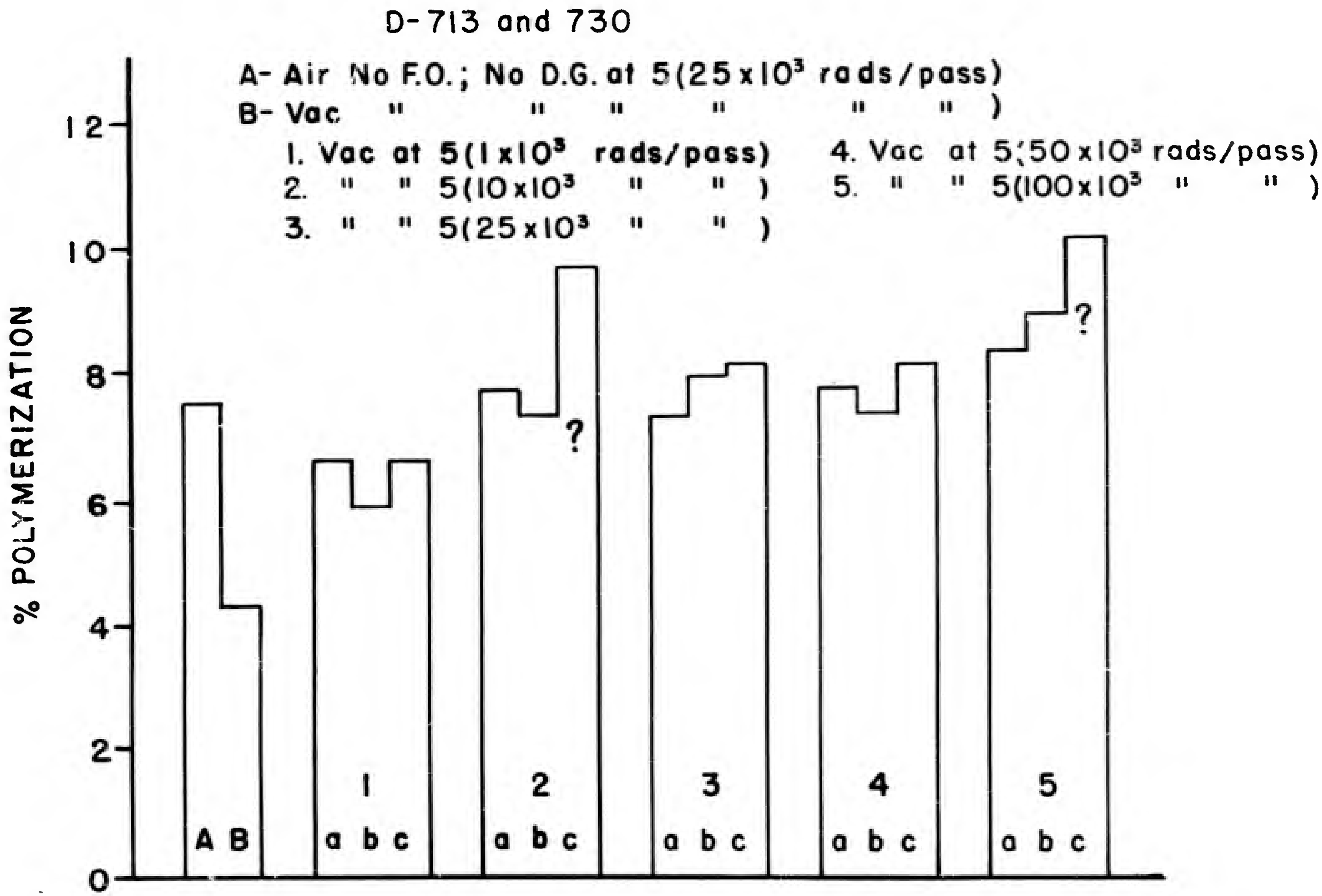


Figure 5. Acrylonitrile-Styrene (1:1, v:v, D-713 and 730): Multiple-Degassing Effect. Values for comparable heat-control samples for A and B are 2.8% and 9.8%.

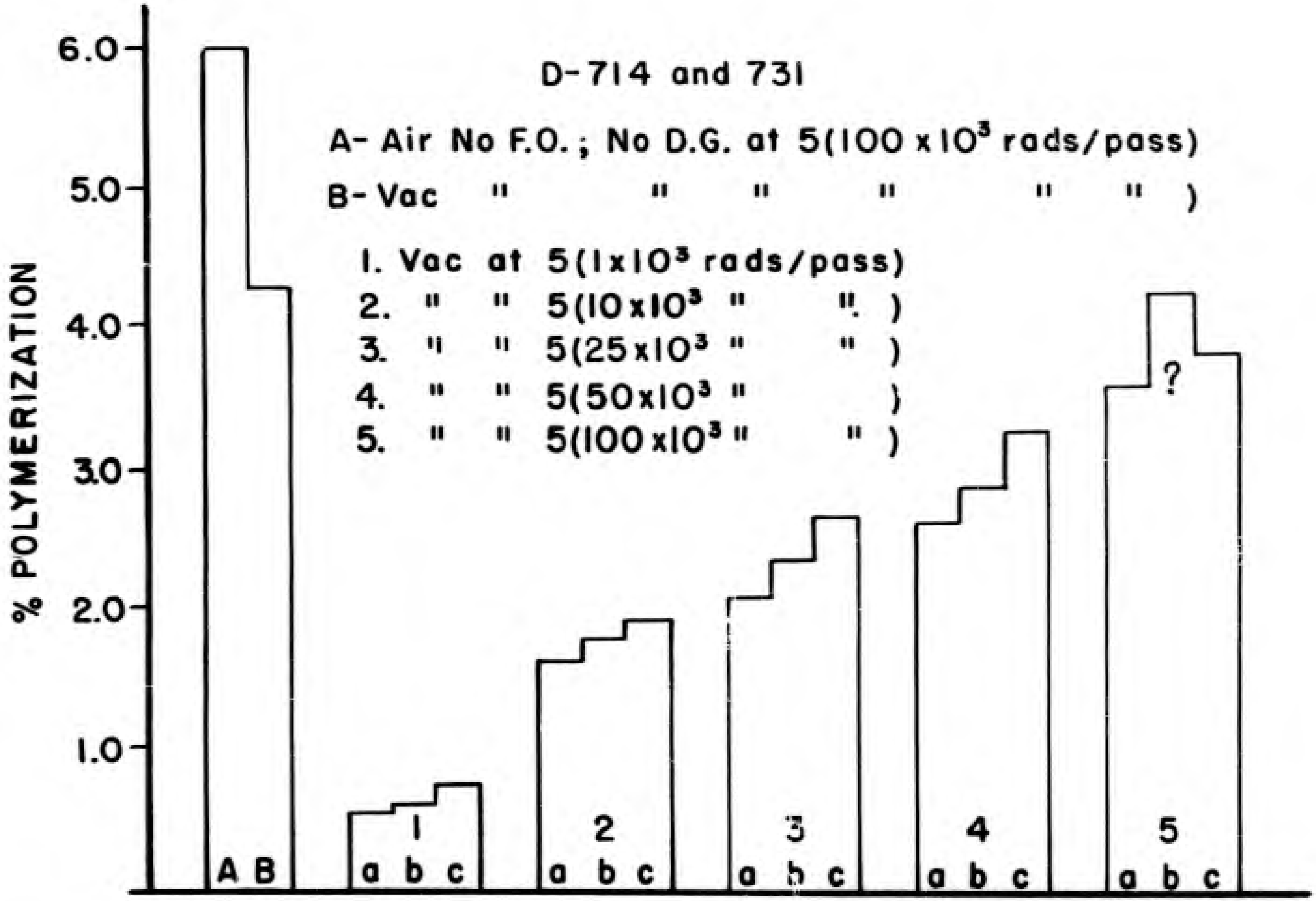


Figure 6. Butyl Acrylate-Styrene (1:1, v:v, D-714 and 731): Multiple-Degassing Effect. Values for comparable heat-control samples for A and B are 0.0% and 0.0%.

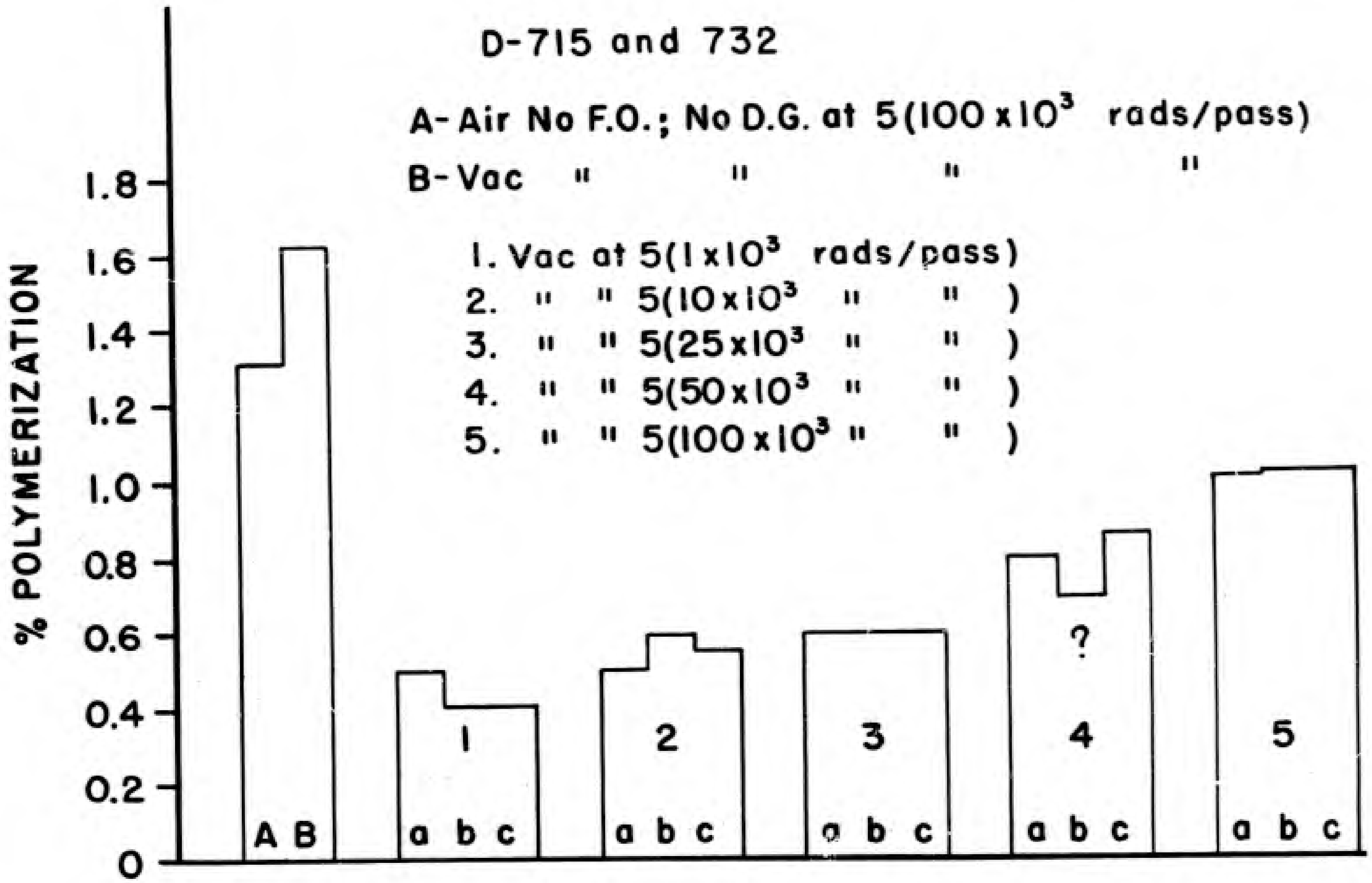


Figure 7. Vinyl Acetate-Styrene (1:1, v:v, D-715 and 732): Multiple-Degassing Effect. Values for comparable heat-control samples for A and B are 0.0% and 0.0%.

important also for optimal polymerization with the parameters used. There are indications, in this and previous reports, that under these experimental conditions, slight variations in parameters such as moisture and atmosphere may prove to be significant. Additional studies are indicated on butyl acrylate.

3. The Styrene Systems:

The percent polymerization of styrene from samples which were subjected to one, two, or three degassings and irradiated at five dose rates and dose levels, is shown by Figure 3 (page 4).

There is an apparent inconsistency in a comparison of the A-bar with the B-bar of Figure 3 and the 1-bar with the 2-bar of Figure 11 (page 16). In the statistical study on the significance of irradiation parameters (Research Report No. 1, page 14, November, 1959), it was found that an air atmosphere is more conducive to polymerization of styrene by use of irradiation than is an air-free system.

The bar graphs of Figure 11 (page 16) confirm those of Figure 3 (page 4), and other observations under these experimental conditions, relative to the effect of degassing on the irradiation-induced polymerization of styrene monomer. Degassings appear to have little or no apparent effect with the other parameters used in this study. The third bar of Figure 11 suggests that a small amount of moisture might be desirable for optimal polymerization of styrene under these conditions. It was reported previously (Research Report No. 3, November, 1960), however, that saturation of styrene with water definitely inhibits the extent of conversion to polymer.

Irradiation at 75°C. results in a much higher conversion to polymer than does that at 25°C. (cf. bars 7 and 8, Figure 11).

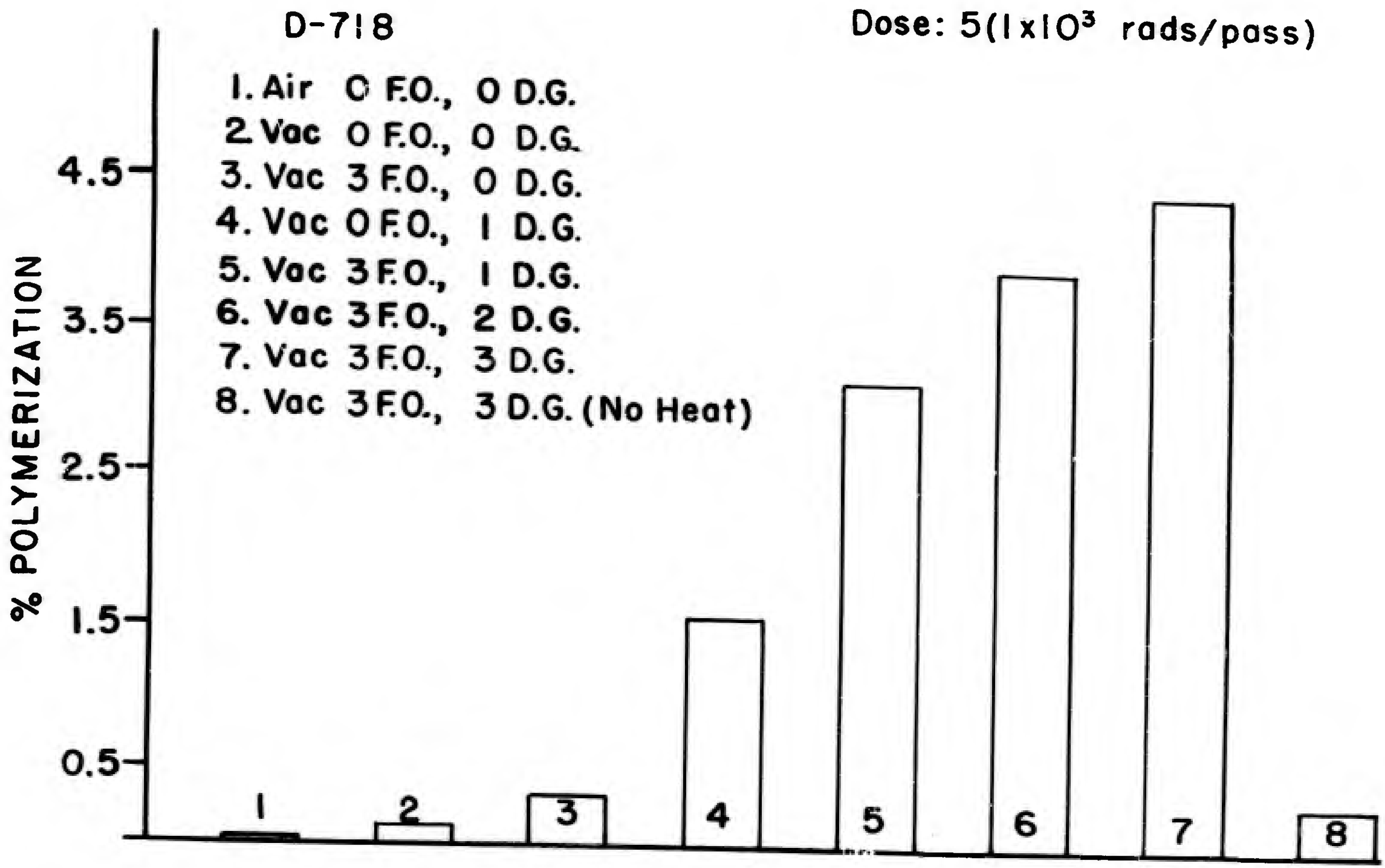


Figure 8. Acrylonitrile (D-718): Multiple Parameters. Comparable heat-control values for 1, 2, and 3 are 0.0%, 0.0%, and 0.0%. Dose: five exposures at 1,000 rads.

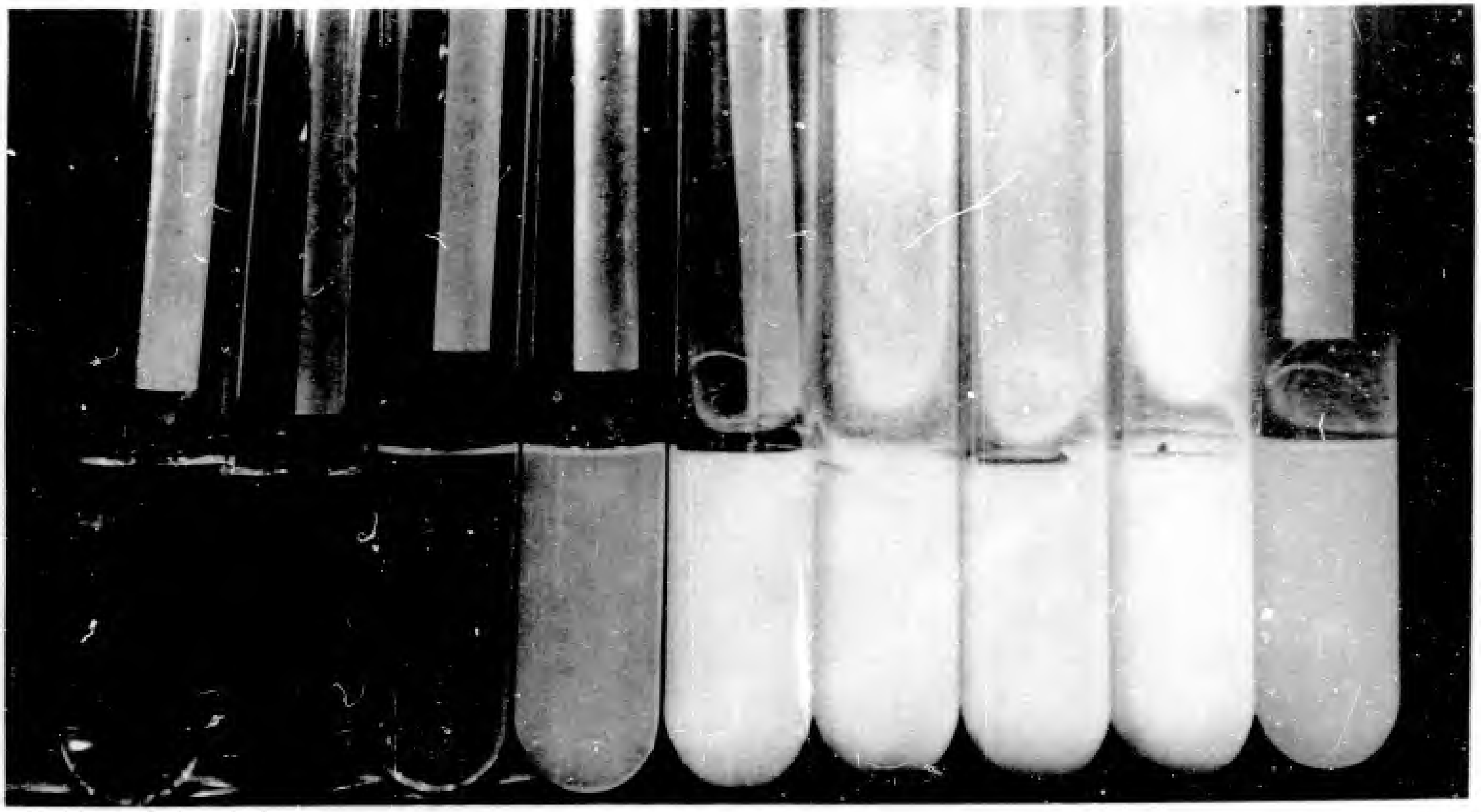


Figure 9. **Acrylonitrile (D-718): Multiple Parameters. Where A is for air, V for** vacuum, F for flame-out, and D for degassed, left to right the samples were prepared as: A,OF,OD, heat control; A,OF,OD; V,OF,OD; V,3F,OD; V,OF,1D; V,3F,1D; V,3F,2D; V,3F,3D; and V,3F,3D (irradiated at 25°C. on a forty-five-minute cycle).

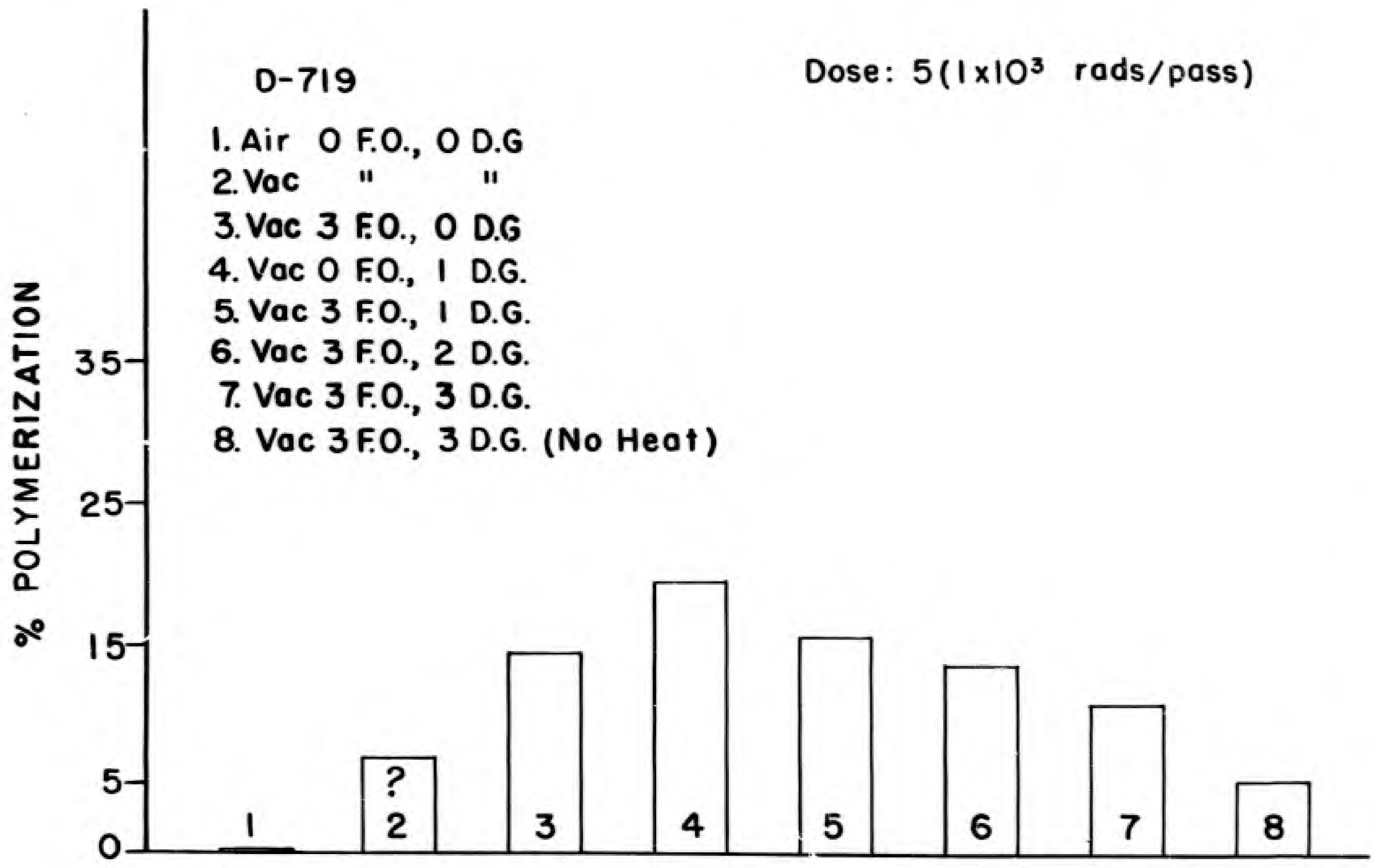


Figure 10. Butyl Acrylate (D-719): Multiple Parameters. Comparable heat-control values for 1, 3, and 7 are 0.1%, 3.8%, and 4.4%. Dose: five exposures at 1,000 rads.

4. The Vinyl Acetate Systems:

The irradiation-induced polymerization of vinyl acetate is increased significantly by the use of an evacuated system, as shown by a comparison of the A- and B-bars of Figure 4 (page 6) and the 1- and 2-bars of Figure 12 (page 18). The effect of degassing is shown by a comparison of the B-bar of Figure 4 for an evacuated sample with the 2-bar of the same figure for degassed samples at the same dose rate and same dose, and the 2-bars of Figures 4 and 12 with the 5-, 6-, and 7-bars of Figure 12. The 2-a-bar of Figure 4 checks with the 5-bar of Figure 12, the 2-b-bar with the corresponding 6-bar, and the 2-c-bar with the 7-bar. There is, accordingly, an increase in the conversion to polymer as the result of one degassing, a further increase at the lower dose rates by the use of a second degassing, and little, if any, change from the use of a third degassing. The combined effect of degassing and heat is evidenced by a comparison of bars 7 and 8 of Figure 12 (page 18), almost three times as much conversion having been obtained at 75°C. as at 25°C.

5. The Acrylonitrile-Styrene Systems:

The results obtained by the irradiation at five dose rates of a mixture of acrylonitrile-styrene (1:1, v:v) in air, in vacuum, and with one, two, or three degassings is given by Figure 5 (page 8). The styrene is dominant with respect to the samples in air and vacuum (cf. Figures 1 and 3, bars A and B). Otherwise there is no well-defined pattern. There was no evidence of a yellow coloration of polyacrylonitrile irrespective of the relatively fast response of acrylonitrile to irradiation as compared to styrene. Further studies are indicated for this mixture.

6. The Butyl Acrylate-Styrene Systems:

The data obtained by the irradiation-induced polymerization of a butyl acrylate-styrene mixture (1:1, v:v) at

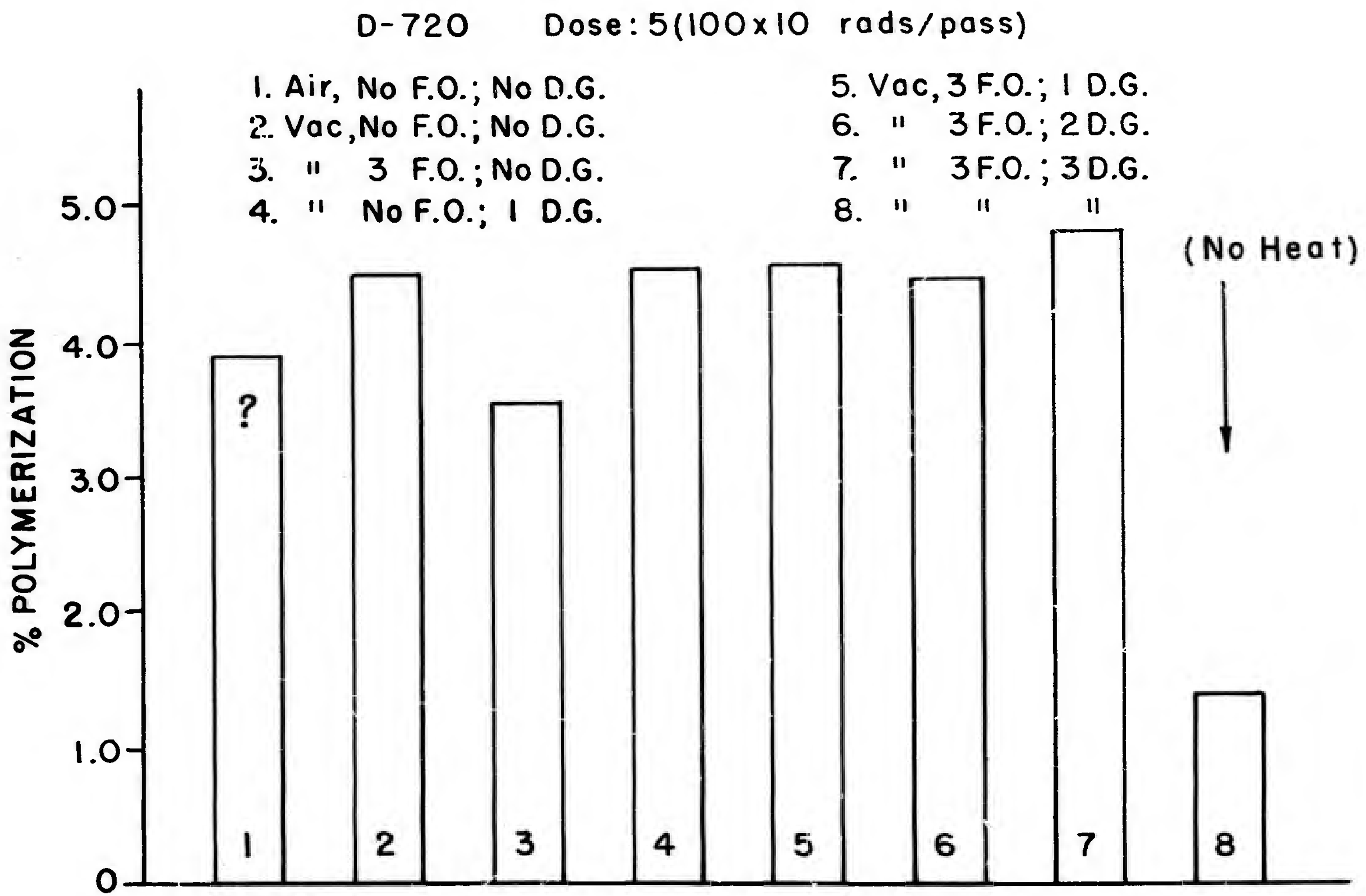


Figure 11. Styrene (D-720): Multiple Parameters. Comparable heat-control values for 1, 3, and 7 are 3.8%, 1.9%, and 2.0%. Dose: five exposures at 100,000 rads.

five dose rates and dose levels, and with one, two, or three degassings, is given by the bar graphs of Figure 6 (page 9). A comparison of the A- and B-bars indicates that the styrene is the dominant member with respect to the use of air or a vacuum system. There is a consistent pattern at dose rates of 1,000, 10,000, 25,000, and 50,000 rads per exposure for the effect of multiple degassing, with a slight but consistent increase in polymer formation. Additional studies on this mixture, however, are indicated.

7. <u>The Vinyl Acetate-Styrene Systems</u>:

The results for the irradiation at five dose rates and dose levels of a mixture of styrene and vinyl acetate (1:1, v:v) are shown as Figure 7 (page 10), and those for five exposures at 100,000 rads as Figure 16 (page 24). A comparison of the A- and B-bars of Figure 7 shows that an evacuated system gives higher conversions of polymer than does an atmosphere of air. There is no apparent significant effect from degassing indicated by either Figure 7 or 16. There is a significant difference, however, in the amount of polymer obtained by use of temperatures of 75°C. and 25°C. (cf. bars 7 and 8, Figure 16).

8. <u>The Acrylonitrile-Vinyl Acetate Systems</u>:

The acrylonitrile-vinyl acetate mixture (1:1, v:v) was given five exposures at 10,000 rads. Eight variations in parameters were used, as indicated on Figure 13 (page 20). There is a consistent increase in polymer formation per unit of radiation energy with a decrease in air and moisture (bars 1 to 7) and heat (bars 7 and 8)

A visual effect of variations in parameters is given by Figure 14 (page 21), although the samples provided a better study than does the photograph. The variations in parameters are given in the legend. The amount of polymer obtained per tube, left to right, was: 0.0%, 0.03%, 0.3%, 0.4%, 0.5%, 0.6%, 0.5%, 0.6%, and 0.2%.

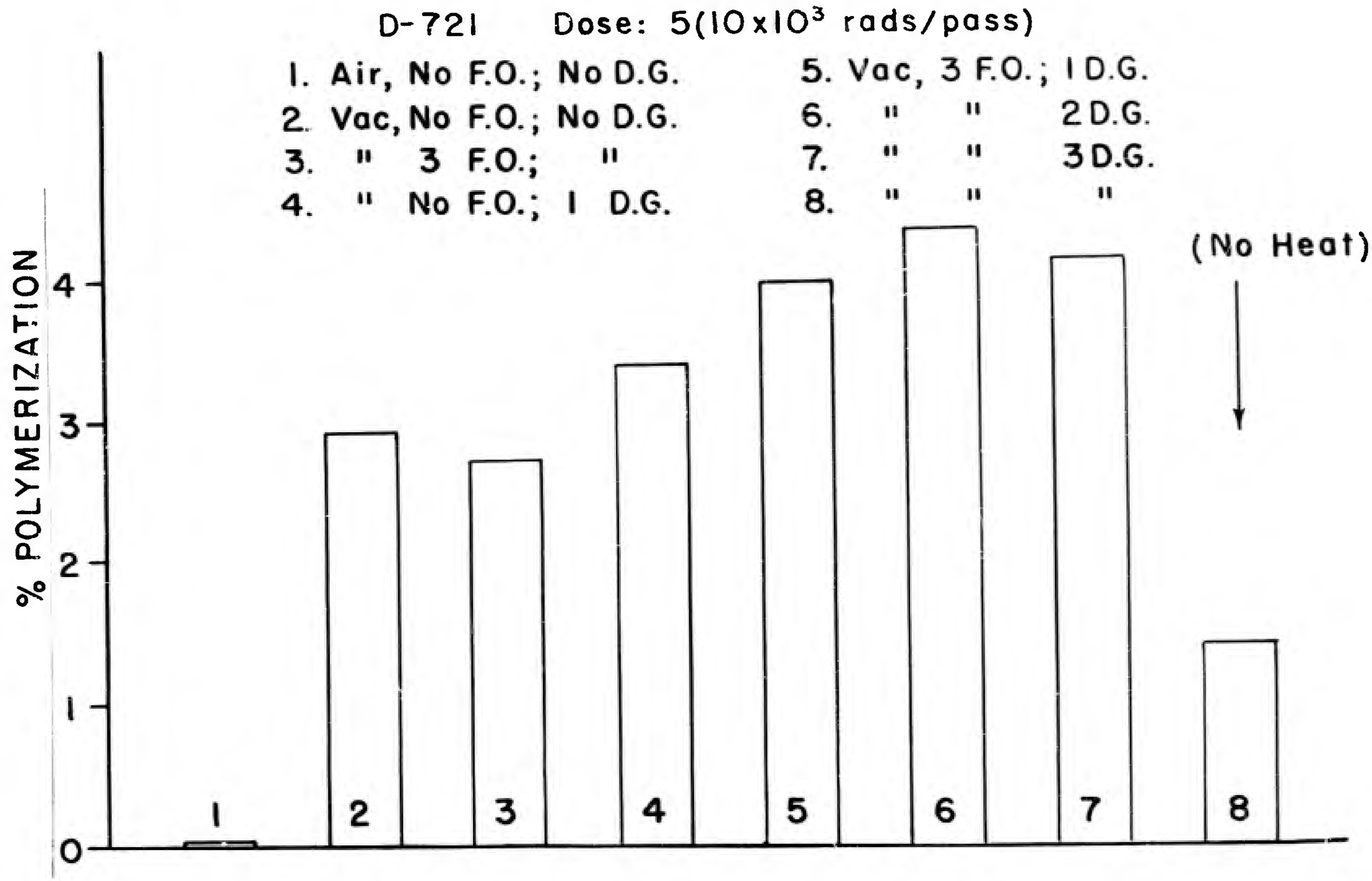


Figure 12. Vinyl Acetate (D-721): Multiple Parameters. Comparable heat-control values for 1, 3, and 7 are 0.0%, 0.0%, and 0.0%. Dose· five exposures at 10,000 rads.

9. The Butyl Acrylate-Vinyl Acetate Systems:

The results for five exposures of a mixture (1:1, v:v) of butyl acrylate and vinyl acetate at 25,000 rads, with eight variations in parameters, are given as Figure 15 (page 22). There is a definite increase in conversion when an evacuated system is used instead of air (cf. bars 1 and 2), but the flame-out of the tubes made no additional contribution to polymer formation per unit of radiation energy, as observed by comparing bar 2 with 3 and bar 4 with 5. There is a consistent increase in conversion to polymer as the degassing step is increased from one to three times. The combined effect of temperature and three degassings is shown by bar 7, the results from a sample irradiated at 75°C., and bar 8 for a comparable sample at 25°C.

10. The 1,1,3-Trihydroperfluoropropyl Acrylate Systems:

Five exposures of samples of 1,1,3-trihydroperfluoropropyl acrylate at 1,000 rads and with eight variations in parameters gave results as shown by Figure 17 (page 25). The presence of air and moisture both inhibit this polymerization as revealed by a comparison of bars 1, 2, and 3. The first degassing evidenced a significant effect (cf. bar 3 with bars 4 and 5), and the second degassing resulted in an increase in polymer formation, whereas the third degassing appears to have had little or no additional effect. The effect of heat is less pronounced in this system than in the others as judged by a comparison of bars 7 and 8 and comparable bars in the other graphs.

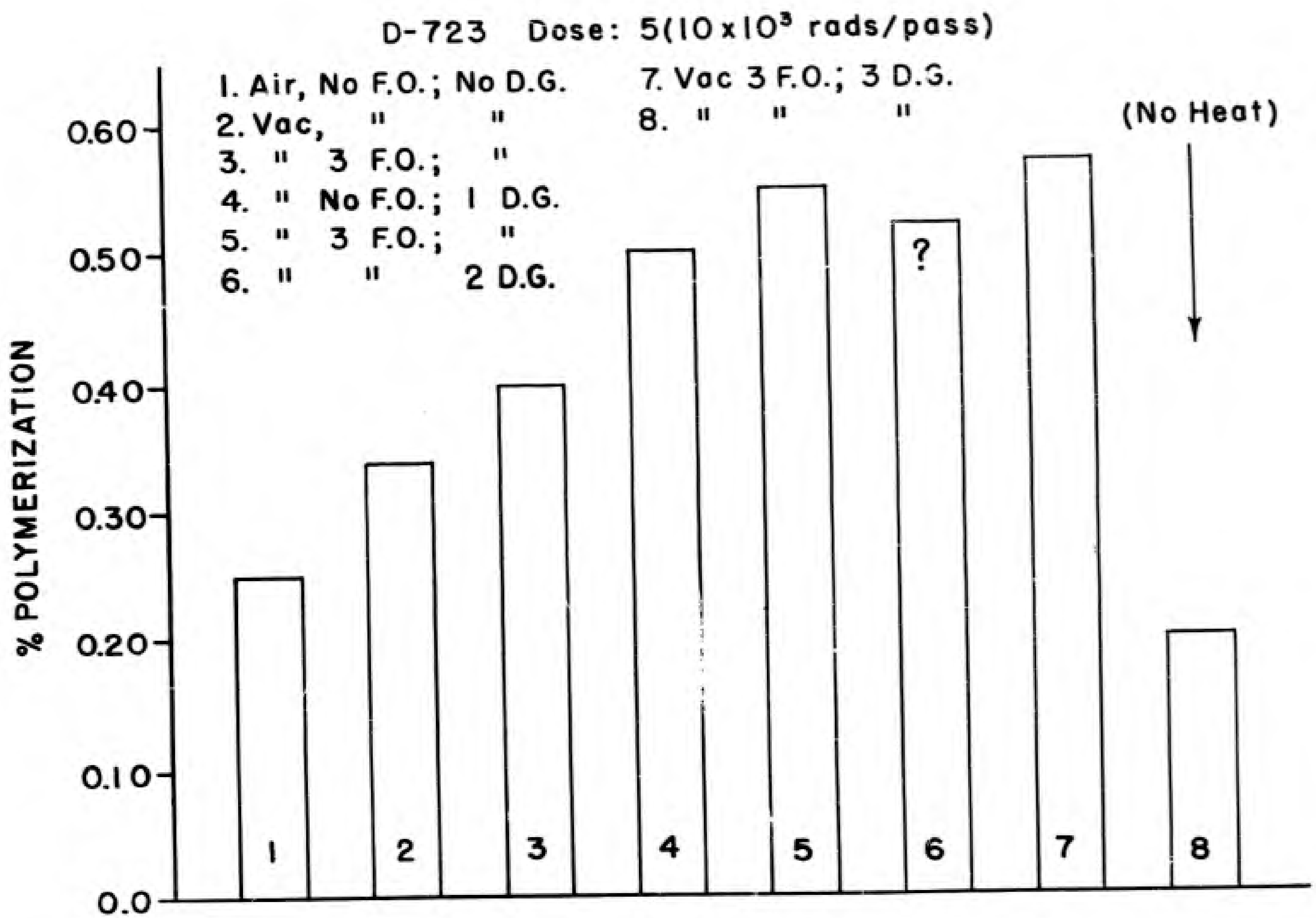


Figure 13. Acrylonitrile-Vinyl Acetate (1:1, v:v, D-723): Multiple Parameters. Comparable heat-control values for 1, 3, and 7 are 0.0%, 0.0%, and 0.0%. Dose: five exposures at 10,000 rads.

Figure 14. Acrylonitrile-Vinyl Acetate (1:1, v:v, D-723): Multiple Parameters. Where A is for air, V is for vacuum, and D for degassed, left to right the samples were prepared as: A,OF,OD, heat control; A,OF,OD; V,OF,OD; V,3F,OD; V,OF,1D; V,3F,1D; V,3F,2D; V,3F,3D; and V,3F,3D (irradiated at 25°C. on a forty-five-minute cycle).

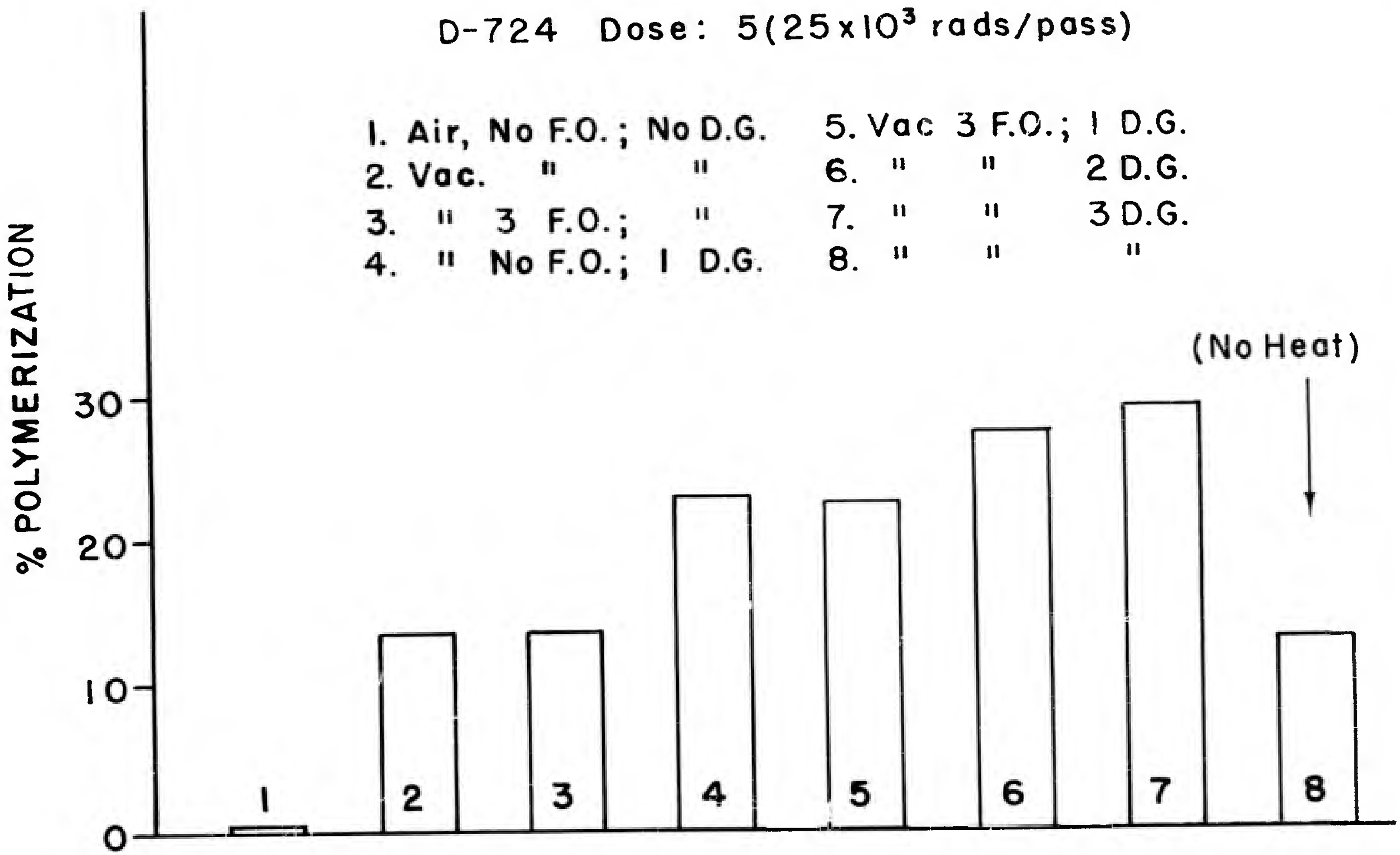


Figure 15. Butyl Acrylate-Vinyl Acetate (1:1, v:v, D-724): Multiple Parameters. Comparable heat-control values for 1, 3, and 7 are 0.0%, 0.0%, and 0.0%. Dose: five exposures at 25,000 rads.

F. Summary

From the data presented in this report it is concluded that the effect of:

1. Air on a degassed system is dependent on the monomer system.

2. Flame-out of the tubes is dependent on the monomer system.

3. Degassing once, twice, or three times is dependent on the monomer system.

4. The combination of flame-out and degassing is also dependent on the monomer system.

5. Heating at 75°C. in combination with three flame-outs and three degassings is significantly more effective in increasing the amount of polymer in the eight systems studied than is the use of a temperature of 25°C. There is observed also from these results an indication, noted previously in studies in this laboratory, that a minimum amount of both moisture and oxygen may be desirable for optimal polymerization of certain monomers with a given set of parameters.

G. Acknowledgments

The authors express their appreciation for the helpful assistance of: (1) Drs. E. D. Black, H. S. Levinson, C. Merritt, Jr., and Charles C. Rainey for reviewing this report, (2) Mrs. Phyllis Zelezny for her painstaking care in the preparation of the copy for reproduction, (3) W. H. Hall, who built the high vacuum system and prepared the sample tubes, and (4) the Exhibits Branch, the Photographic Section, and the Reproduction Branch for their respective contributions.

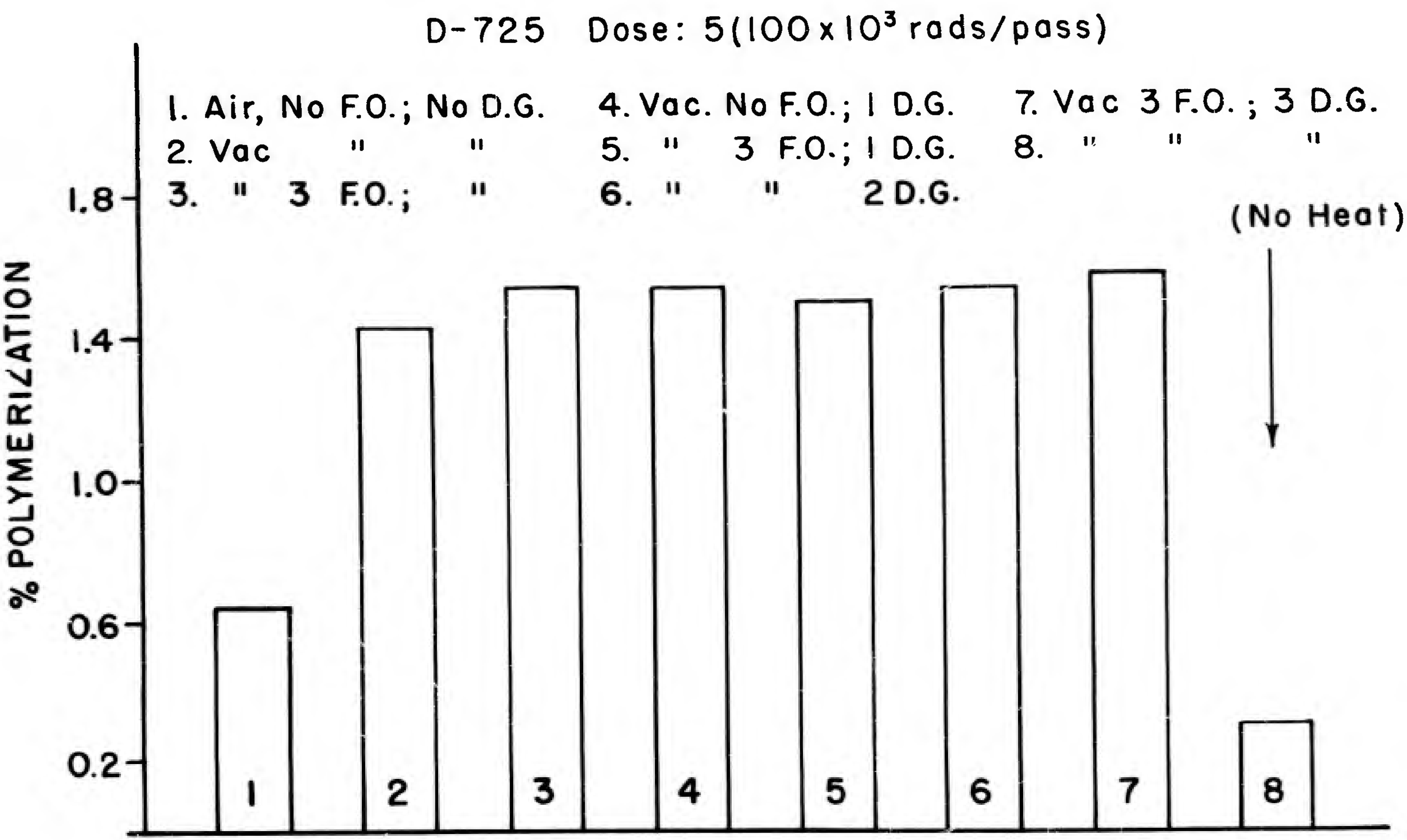


Figure 16. Styrene-Vinyl Acetate (1:1, v:v, D-725): Multiple Parameters. Comparable heat-control values for 1, 3, and 7 are 0.0%, 0.0%, and 0.0%. Dose: five exposures at 100,000 rads.

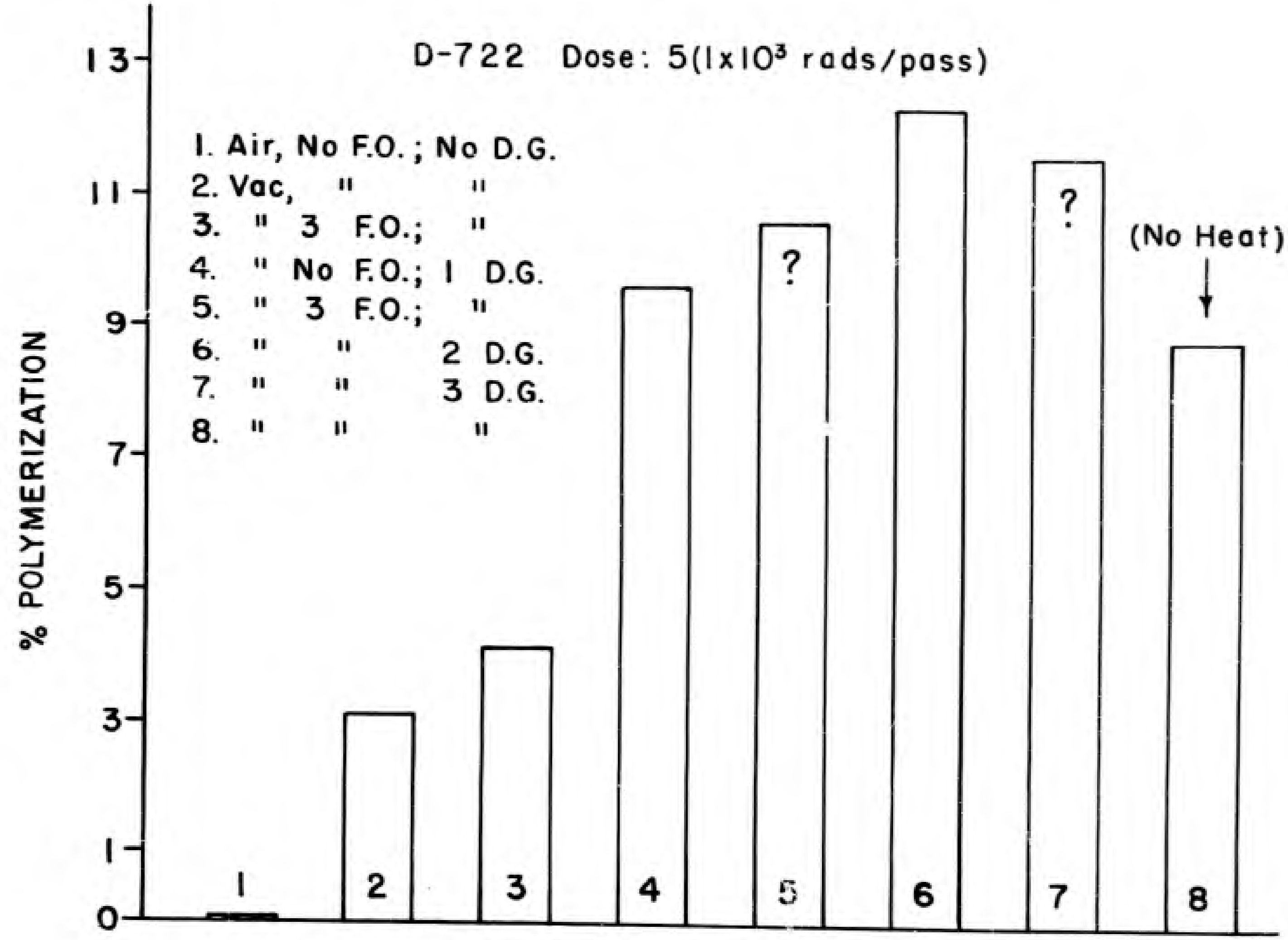


Figure 17. 1,1,3-Trihydroperfluoropropyl Acrylate (D-722): Multiple Parameters. Comparable heat-control values for 1, 3, and 7 are 0.0%, 0.0%, and 0.0%. Dose: five exposures at 1,000 rads.

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